APPENDIX I.

RESTRICTED MATERIALS PERMIT, NOI and PESTICIDE USE REPORT

GLENN COUNTY DEPARTMENT OF AGRICULTURE
720 N. COLUSA ST. (P.O. BOX 351)
WILLOWS, CALIFORNIA, CA 95988
Office: (916)934-6501 Recorder (NOI) (916)934-6501 FAX: (916)934-6503

RESTRICTED MATERIALS PERMIT

PERMIT/OPERATOR I.D. #: 11-94-04008
County HQ District #:
Expiration Date: 01/24/9
Issue Date: 01/24/9

KEYAWA ORCHARDS INC.
P.O. BOX 8270
CHICO, CA 95927-

DAVE KEYAWA E
P.O. BOX 8270
CHICO, CA 95927

Home: (916)826-33
Shop: (916)826-33
Mobile: (916)520-05

FOR RESTRICTED MATERIALS PERMIT USE ONLY

Permit Type: Poss. Only [ ] Seasonal [X] Poss. & Use [X] Job
Permittee Type: O.A. Cert [X] Ag. PCO [ ] Private App [ ] Non-Ag
NOI required 24 hours prior to application.
Method: phone [X] box [ ] person [X] modem [ ] fax

Numb	Pesticide	Pest(s)	Form.	Method(s)		Applicator(s)	
0351	SEVIN	worms	Wettable	Air	Ground	PCO	Grower
0101	TRITHION	Hornfly	Liquid	Air	Ground	PCO	Grower
2010	DIURON	weeds	Liquid	Ground		Grower	
0191	THIODAN	Aphids	Liquid	Air	Ground	PCO	Grower
2580	ETHION	Codlingmoth	Liquid	Air	Ground	PCO	Grower
2140	AZINPHOS-METHYL	w/Codlingmoth	Liquid	Ground		PCO	Grower
3250	METHYL BROMIDE	Nematodes	Fumigant	Ground		PCO	Grower
4820	PHOSPHAMIDON	Heat Fly	Liquid	Air	Ground	PCO	Grower
4442	PHOSTOXIN	Squirrels	Fumigant	Fumigate		Grower	
5310	SIMAZINE	weeds	Liquid	Ground		Grower	
5540	STRYCHNINE	Gophers	Bait	Ground		Grower	
5250	ZINC PHOSPHIDE	Squirrels	Bait	Ground		Grower	
5360	2,4-D	Blueweed	Liquid	Ground		PCO	Grower
12750	2,4-D, PROPYL E	"	Liquid	Ground		Grower	

*** Pesticides continued on next page ***

Non-Ag Use:
Conditions: ALL

I understand that this permit does not relieve me from liability for any dam to persons or property caused by the use of these pesticides. I waive any claim of liability for damages against the County Department of Agriculture based on the issuance of this permit. I further understand that this permit may be revoked when pesticides are used in conflict with the manufacturer's labeling or in violation of applicable laws, regulations and specific conditions of this permit. I authorize inspection at all reasonable times a whenever an emergency exists, by the Department of Pesticide Regulation or t County Department of Agriculture of all areas treated or to be treated, stor facilities for pesticides or emptied containers and equipment used or to be used in the treatment. [Form 33-125/v3.53 (Rev. 02/15/90) Pesticide Enforcem ranch]

Permit Applicant: Dave E Keyawa Sign: _____

Title: Supervisor Date: 1/24/94

Issuing Officer: Laura B Mendenhall Date: 1/24/94

A ORCHARDS INC. Permit #: 11-94-0400855
cides continued:

mb	Pesticide	Pest(s)	Form.	Method(s)		Applicator(s)	
111	PARAQUAT	weeds	Liquid	Ground		Grower	
891	SUPRACIDE	Scale Carp	Liquid	Air	Ground	PCO	Grower
881	AMBUSH	NAVEL Moth	Liquid	Air	Ground	PCO	Grower
882	POUNCE		Liquid	Air	Ground	PCO	Grower
941	ASANA clofentezine		Liquid	Air	Ground	PCO	Grower
~~990~~	~~SIFENTHRIN~~	Mites	Liquid	Ground		Grower	
999	NON-PERMIT AG P	Vectors Blight	Liquid	Air	Ground	PCO	Grower

90 March

ployees handle pesticides (Y or N) |Y|

ntact People:	Phone	PCO	PCA	PCD	Other
AG	~~(916)865-9606~~	X			
LENA SDAHLMAN ADV	(916)343-5881			X	
EMTEC	(916)345-6148			X	
RK KEENAN	(916)345-6148		X		
PLOT	(916)865-9661			X	
RTY CULLIN	(916)865-9661		X		

mb	Site #	Dist	Sect	Town	Range	Mer	Quant	Unit	Cond
UNOS	6	4	30	21N	01W	M	16.00	A	ALL
001-0)	SITE 6 M4					G & D RANCH W/RDXX & N/RD 30.5			
	1051, 1101, 5540, 6360, 16011, 16891, 20081								
	7	3	17	19N	01W	M	40.00	A	ALL
	SITE 7 M5					K & C RANCH 1.8 MILE NW Y &162			
	1051, 1101, 5540, 6360, 16011, 16891, 20081								
NUTS	3	3	20	18N	01W	M	118.00	A	ALL
009-0) X	SITE 3 M3					S/RD 69 & BTWN/XX			
	1051, 1101, 2310, 2591, 2680, 3140, 3850, 4820, 6360, 16011								
	16891, 99999								
	4	1	17	21N	03W	M	145.00	A	ALL
	SITE 4 M6					N/RD 28 AND RD F			
	1051, 1101, 2310, 2591, 2680, 3140, 3850, 4820, 6360, 16011								
	16891, 99999								
	5	4	30	21N	01W	M	16.00	A	ALL
	SITE 5 M4					G & D RANCH W/RDXX & N/RD 30.5			
	1051, 1101, 2310, 2591, 2680, 3140, 3850, 4820, 6360, 16011								
	16891, 99999								
	8	3	17	19N	01W	M	40.00	A	ALL
	SITE 8 M5					K & C RANCH 1.8 MILE NW Y &162			
	1051, 1101, 2310, 2591, 2680, 3140, 3850, 4820, 6360, 16011								
	16891, 99999								
COL NON-AG	1	4	29	21N	01W	M	30.00	A	ALL
7000-0)	SITE 1 M1					1/4 MI E/HWY 45 S/30 1/2			
	6360, 16011, 99999								

TO: GLENN CO (916) 934-6503

FROM: AVAG, INC. (916)882-4543
STIONS CALL: 882-4286

NOTICE OF INTENT - GLENN COUNTY

APPLICATOR AVAG	Date 7-26-94	Submitted by MVC	Permittee KEYANA	Permit # 0400855
Commodity WALNUTS	Pests BUGS		Hazards/changes NO	Ap.Date 7-29-94

Site #	Acres	Location	Pesticide	Rate	Dilution
3/3	116.	S/RD 69 & BTWN XX	GUTHION	4#	30
			Start Time		
			6:30 - 10:00 AM		

APPLICATOR AVAG	Date	Submitted by	Permittee	Permit #
Commodity	Pests		Hazards/changes	Ap.Date

Site #	Acres	Location	Pesticide	Rate	Dilution

STATE OF CALIFORNIA
DEPARTMENT OF FOOD AND AGRICULTURE

PESTICIDE USE REPORT

12718

NURSERY

1 COUNTY NO.	2 SECTION	3 TOWNSHIP N	4 RANGE E	5 BASE & MERIDIAN	6 APP. METHOD	7 PERMITTEE/PROPERTY OPERATOR
11	20	18N S	01W W	M	AIR	KEYAMA ORCHARDS

APPLICATOR NAME AND ADDRESS
AVAG, Inc 12477
P.O. Box 156
Richvale, CA

8 OPERATOR ID/PERMIT NO.	9 SITE IDENTIFICATION NUMBER	10 TOTAL PLANTED ACRES/UNITS	12 BLOCK ID (IF APPLICABLE)
11-94-0400855	3 3	118.00	

11 LOCATION: S/RD 69 & BTWN/XX

14 DATE/TIME APPLIED	15 ACRES/UNITS TREATED	16 COMMODITY/SITE TREATED	
7/29/94 730	116.00	WALNUT	03009-00

17 CHEM. NO.	18 MANUFACTURER/NAME OF PRODUCT APPLIED	19 EPA/CALIF. REG. NO. FROM LABEL	20 TOTAL PRODUCT USED	21 RATE	22 DILUTION
	GUTHION 50W MILES, INC.	3125-301-AA	464.00 LB LB. OZ. PT. QT. GA.	4.00 LB	30
			LB. OZ. PT. QT. GA.		
			LB. OZ. PT. QT. GA.		
			LB. OZ. PT. QT. GA.		
		[illegible]	LB. OZ. PT. QT. GA.		
		[illegible]	LB. OZ. PT. QT. GA.		

24 DAYS REENTRY	25 DAYS PREHARVEST	26 APPLIED/SUPERVISED BY
		OLSSON,

[illegible] within 7 days of application

33-028 (REV. 3/90) 90 91243

APPENDIX II

ANALYTICAL S.O.P.

Method NLS015

Standard Operating Procedure for the Determination of Azinphos Methyl in Ambient Air

1. SCOPE

This document describes a method for the analysis of azinphos methyl (Guthion, O,O-Dimethyl-S-[4-OXO-1,2,3-benzo-triazin(4H)-y1 methyl] phosphorodithioate) at concentrations normally found in ambient air. The method was developed based on EPA and California Department of Food and Agriculture methods.

2. SUMMARY OF METHOD

After sampling, the exposed tefion filter and XAD-2 sorbant tube are desorbed with 2.0 milliliters of 80/20 isooctane/acetone mixture. Two microliters of the extract are injected using splitless mode technique into a gas chromatographic system equipped with a 12 meter DB-1 fused silica capillary column, N-P thermionic detector (TSD), and data system. The resultant peak is identified by a characteristic retention time and quantitated in reference to external standards. The identity of the component can be confirmed by use of a column of different characteristics, a detector of different selectivity, or, if sufficient material is present, by GC/MS.

3. INTERFERENCES/LIMITATIONS

3.1 Since sampling is outside the scope of this document, sampling techniques, equipment, and conditions will not be discussed. Sampling capture efficiency studies have not been performed for the preparation of this SOP.

3.2 Compounds responding to the TSD detector and having similar GC retention times may interfere, causing misidentification and/or erroneous quantitation.

3.3 To insure minimum losses during storage, all samples received by the laboratory must be placed in a freezer operating at -4 degrees Centigrade or lower.

4. APPARATUS

4.1 Varian Model 3300 Gas Chromatograph equipped with a thermionic detector (TSD) and Spectra Physics Model 4270 integrator.

4.2 DB-1 fused silica capillary column, 12 meters x 0.25 mm I.d., 0.5 um film thickness.

4.3 Glass desorption vials, 3.7 ml capacity, with teflon-lined septum caps.

4.4 Sample agitator with timer and sample rack.

4.5 Microliter syringes, 5-50 ul sizes.

5. REAGENTS

5.1 80/20 isooctane/acetone desorbant solvent: Mix 800 ml pesticide grade isooctane (trimethyl pentane) and 200 ml pesticide grade acetone in a clean amber glass bottle equipped with a teflon-lined screw cap. Add to this mixture 1 ml of 2.0 mg/ml benzoxylidine surrogate mixture. CAUTION: FLAMMABLE.

5.2 Surrogate Mixture: Dissolve 100 mg of ACS Grade benzoxylidine in pesticide grade acetone and dilute to 50.0 ml.

5.3 Stock Standard: Commercially available certified solution of 1000 ug/ml of azinphos methyl in methanol (Nanogens, Inc.).

5.4 Calibration Standard: Dilute 50 ul of the stock standard into 50.0 ml of desorbant solvent. This corresponds to 1.0 ug/ml.

5.5 Control Sample: Dilute 10 ul of stock standard into 50.0 ml of desorbant solvent. This corresponds to 0.2 ug/ml.

6. INSTRUMENT CONDITIONS

Column: 12 m x 0.25 mm i.d. DB-1 fused silica capillary column

Temperatures: Injector: 250 degrees Centigrade

Detector: 300 degrees Centigrade

Oven: 50 degrees Centigrade, initial; hold for 1 minute; ramp at 50 degrees Centigrade to 150 degrees Centigrade; ramp at 10 degrees Centigrade/minute to 250 degrees Centigrade, hold for 4 minutes

Flow Rates: Carrier: Helium, 30 cc/minute at splitter, 0.8 minutes splitless hold, carrier velocity; 25 cm/second

Detector: TSD - Range 11, Attenuation x 1

Hydrogen: 4.5 cc/minute

Air: 200 cc/minute

7. INSTRUMENT CALIBRATION PROCEDURE

7.1 Before a standard solution can be analyzed, a system blank must be analyzed. Inject 2.0 ul of solvent. If the analysis indicates interferences or contamination, the solvent must be replaced and the problem solved.

7.2 A method blank must be analyzed every 12 samples. Select an unused filter and sorbant tube, desorb the blank samples and carry through the analysis procedure. If inteferences or contamination is noted, the source must be found and eliminated before the analysis of samples can continue.

7.3 Instrument calibration is performed by injection of 2.0 ul of the 1.0 ug/ml standard. The resultant chromatogram is used to calibrate the retention time and response factor of the azinphos methyl under the conditions of this procedure. Calibration standards must be run every 12 samples.

7.4 Proper instrument calibration is checked by the analysis of a control sample. The control sample must be analyzed after each calibration and prior to the analysis of samples. The concentration resulting from this analysis must fall within the upper and lower warning limits ($\pm 2\sigma$) of the control sample known value. If a result falls outside these limits, the problem must be found and solved prior to the analysis of samples. Plot all control sample results on the method control chart.

7.5 Two unused sampling media are "spiked" with 1.0 ug of azinphos methyl for each group of samples received by the laboratory. These method spikes must be carried through the analytical procedure with the field samples. Method recovery must be at least 80%.

8.0 ANALYSIS OF SAMPLES

8.1 Remove the teflon filter from the filter holder with stainless steel forceps. Carefully roll the filter and place it into a 3.7 ml vial. The filter must be forced into the bottom of the vial with a clean glass rod to insure complete contact with the solvent.

8.2 After removal of the end-caps from the sorbant tube, score the tube above the location of the retainer spring. Using the tool provided, break the tube and remove the retainer spring. Place the glass wool plug and the primary (400 mg) section of the sorbant into a 3.7 glass vial. Retain the secondary section for later analysis in the event that the analyte is detected in the primary section.

8.3 Place 2.0 ml of desorbing solvent into all vials, cap tightly and agitate for 45 minutes.

8.4 After desorption, inject 2.0 ul of each extract into the chromatographic system for analysis. Record all pertinent information in the instrument analysis log book and on the resultant chromatogram.

8.5 The results are recorded in micrograms per sample and are calculated as follows:

micrograms = ug/ml (found) x 2 ml

9.0 METHOD SENSITIVITY, PRECISION AND ACCURACY

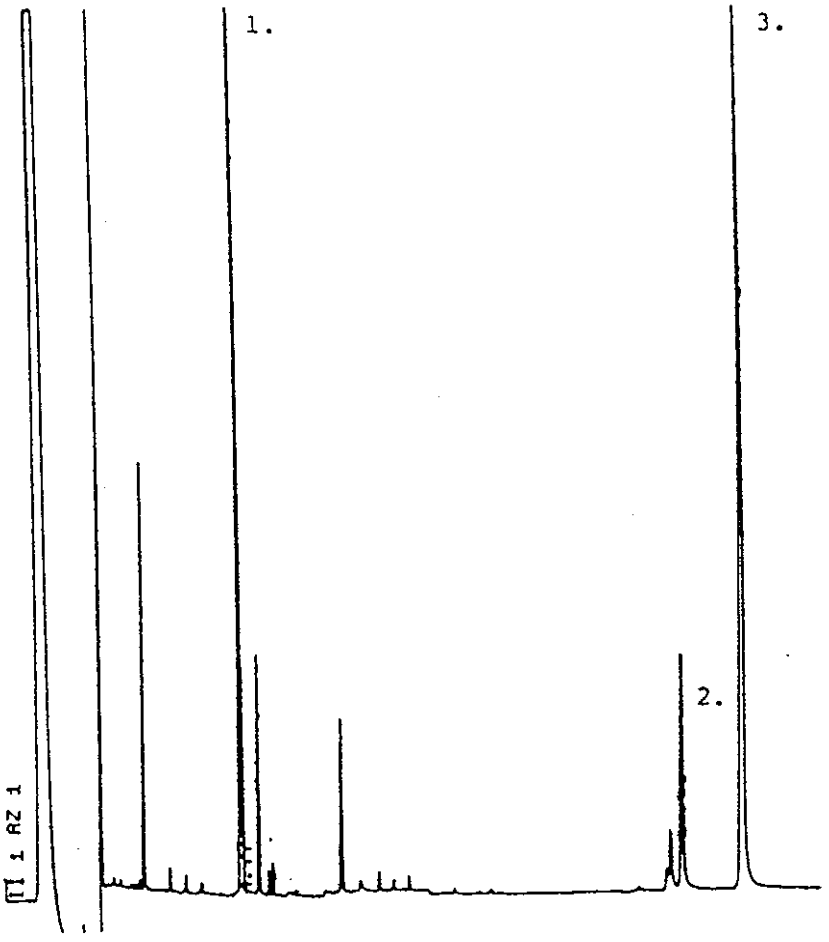
The method sensitivity, precision and accuracy are presented in Table 1. The data were generated using standards. Note that the MDL is presented in ug/ml and in ug/sample assuming a desorption volume of 2.0 ml. A sample chromatogram is shown in Figure 1.

10.0 DESORPTION EFFICIENCIES AND SAMPLE STABILITY

The primary section of XAD-2 sorbant tubes were spiked with 2.0 and 1.0 micrograms of azinphos methyl. Five each of the tubes were analyzed immediately to determine desorption efficiencies. Five each of the tubes were stored for ten days at -4 degrees Centigrade and analyzed. The results are shown in Table 2.

FIGURE 1

AZINPHOS METHYL STANDARD CHROMATOGRAM



2.0 ul injection of 1.0 ug/ml azinphos methyl standard; splitless mode; 12m X 0.25mm i.d. DB-1 capillary column, 50°C, 1 min., 50°C/min to 150°C, 10°C/min to 250°C, 25cm/sec He, TSD @ 3.2 amps. Compounds: (1) Surrogate, (2) Azinphos methyl oxon, (3) azinphos methyl

TABLE 1

METHOD PRECISION, ACCURACY, AND SENSITIVITY

Azinphos Methyl, ug/ml	1.0	0.5	0.2	0.1
Relative Standard Deviation, %	9.6	8.8	11.0	4.8

Correlation Coefficient:	0.998	
Slope:	0.976	
Intercept:	0.021 ug/ml	
Method Detection Limit:	0.035 ug/ml	(0.07 ug/sample)

TABLE 2

SAMPLE STABILITY AND DESORPTION STUDIES

Desorption Efficiencies:	2.0 micrograms/sample:	88 ± 9 %	n=5
	1.0 micrograms/sample:	86 ± 10 %	n=5

Recovery After Storage At -4°C (10 days):

2.0 ug/sample:	92 ± 10 %	n=5
1.0 ug/sample:	87 ± 9 %	n=5

APPENDIX III

SAMPLING PROTOCOL

State of California

AIR RESOURCES BOARD

PESTICIDE MONITORING PROTOCOL

Application Site Monitoring of Azinphos Methyl in Glenn County during the Summer 1994

Engineering Evaluation Branch

Monitoring and Laboratory Division

Project No. C93-061A

Date Revised: July 28, 1994

APPROVED:

_____, Project Engineer
Testing Section

_____, Manager
Testing Section

_____, Chief
Engineering Evaluation Branch

This protocol has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

July 28, 1994

Protocol for Azinphos Methyl Monitoring in Glenn County
during the Summer 1994

I. Introduction

At the request of the California Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) will conduct source impacted application site monitoring for azinphos methyl in Glenn County. The monitoring is in support of the DPR toxic air contaminant program. Section 14022(c) of the Food and Agriculture Code requires the ARB "to document the level of airborne emissions .... of pesticides which may be determined to pose a present or potential hazard..." when requested by the Department of Pesticide Regulation. This monitoring will be conducted near a specific application, prior to, during, and following an application of this pesticide. Azinphos methyl is an organophosphate insecticide used to control pests on a wide variety of crops: fruits, melons, vegetables, nuts, field crops, ornamentals and shade trees. The target crop for this application is walnuts.

II. Sampling

Calibrated rotometers will be used to set and measure sample flow rates. The flow rate will be approximately 2 liters per minute. Samplers will be leak checked prior to and after each sampling period with the sampling media, XAD-2 resin tubes, installed. Any change in the flow rates will be recorded in the field log book. The field log book will also be used to record start and stop times, sample identifications and any other significant data, including field size, application rate, formulation, method of application, and length of application. The Notice of Intent or Pesticide Use Recommendation will also be obtained for inclusion in the final report.

A meteorological station will be set up to determine wind speed and direction. This station will continue to operate throughout the sampling period. Weather data will also be collected from the nearest California Irrigation Management Information System (CIMIS) station. These data will be included in the final report.

Prior to application, background samples will be taken to establish if any azinphos methyl is detectable. Samples will be collected with XAD-2 resin tubes using battery powered pumps (ATTACHMENT I). Four samplers will be used; one on each side (assuming a rectangular field) of the field at a distance of approximately 15 yards. These distances are approximate and dependent on the physical obstacles surrounding the field. As closely as feasible, the sample tubes will be changed according to the schedule outlined in ARB's "Quality Assurance Plan for Pesticide Monitoring" (ATTACHMENT II).

III. Analysis

The analysis will be conducted by staff of the ARB Engineering Evaluation Branch in Sacramento. All samples will be stored in an ice chest containing either dry ice (if available) or wet ice while in the field and in a freezer at the laboratory until analysis. Analysis of samples will be by gas chromatograph/nitrogen-phosphorus detector (GC/NPD) following extraction of the XAD-2 tube with an 80:20 mixture of isooctane and acetone. The Standard Operating Procedure (S.O.P.) for the analysis of azinphos methyl will be included in the final report.

IV. Quality Assurance

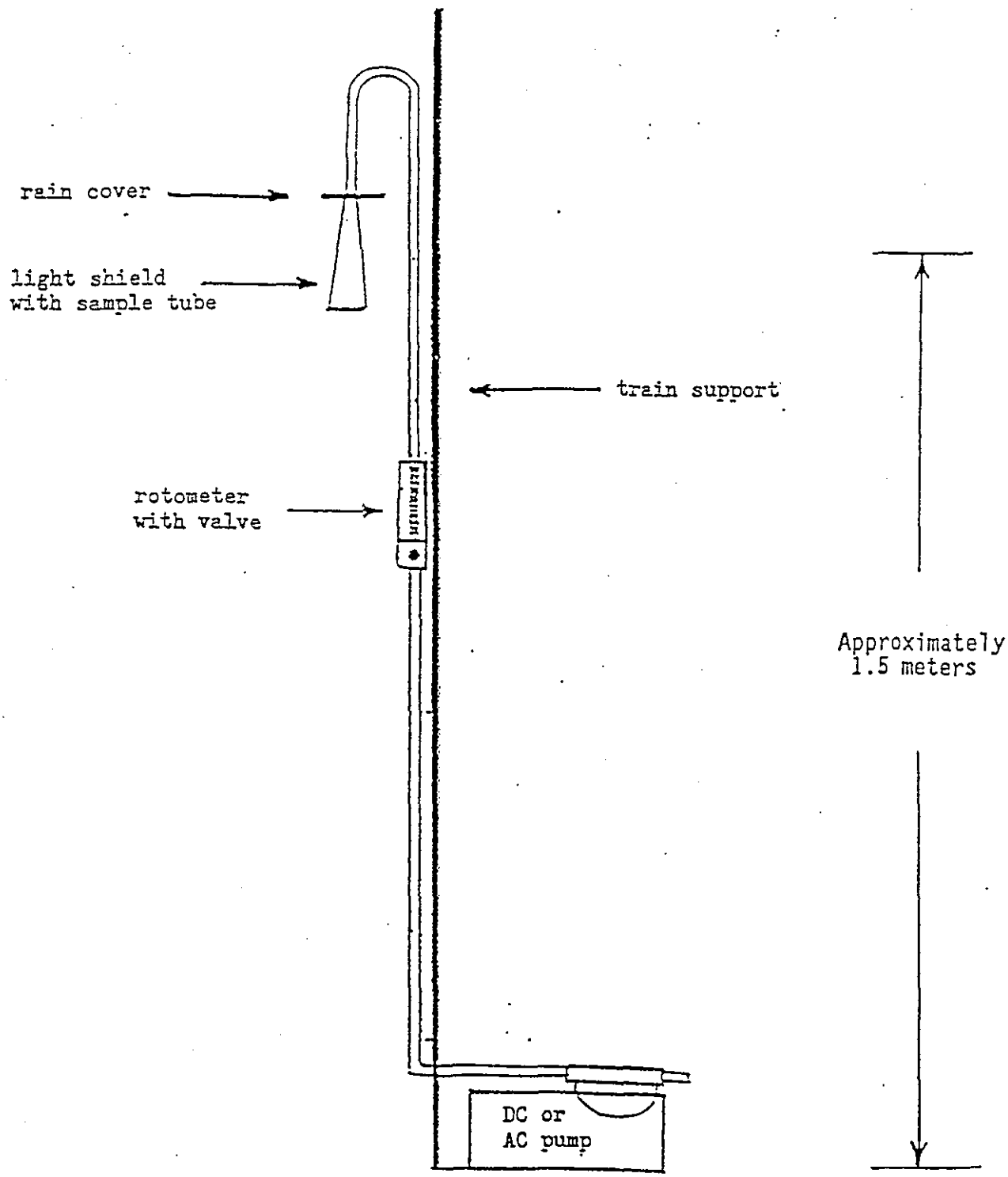
Procedures will follow ARB's "Quality Assurance Plan for Pesticide Monitoring." The instrument dependent parameters (reproducibility, linearity and minimum detection limit) will be checked prior to analysis. A chain of custody sheet will accompany all samples. Sample flow rates will be calibrated prior to and after sampling in the field.

V. Personnel

ARB personnel will consist of Don Fitzell (Project Engineer) with Jack Rogers and LaJuan Taylor (Instrument Technicians).

ATTACHMENT I

PESTICIDE MONITORING APPARATUS


rain cover
light shield
with sample tube
train support
rotometer
with valve
DC or
AC pump
Approximately
1.5 meters

ATTACHMENT II

QUALITY ASSURANCE PLAN FOR PESTICIDE MONITORING

State of California
California Environmental Protection Agency
Air Resources Board

QUALITY ASSURANCE PLAN

FOR PESTICIDE MONITORING

Prepared by the

Monitoring and Laboratory Division

and

Stationary Source Division

Revised: February 4, 1994

APPROVED:

Geneviève Shiroma, Chief
Toxic Air Contaminant
Identification Branch

_____, Chief
Quality Management and Operations
Support Branch

_____, Chief
Engineering Evaluation Branch

This Quality Assurance Plan has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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APPENDIX

QUALITY ASSURANCE PLAN FOR PESTICIDE MONITORING

I. Introduction

At the request of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) documents the "level of airborne emissions" of specified pesticides. This is usually accomplished through two types of monitoring. The first consists of one month of ambient monitoring in the area of, and during the season of, peak use of the specified pesticide. The second is monitoring near a field during and after (up to 72 hours) an application has occurred. These are referred to as ambient and application monitoring, respectively. To help clarify the differences between these two monitoring programs, ambient and application are highlighted in bold in this document when the information applies specifically to either program. The purpose of this document is to specify quality assurance activities for the sampling and laboratory analysis of the monitored pesticide.

A. Quality Assurance Policy Statement

It is the policy of the ARB to provide DPR with as reliable and accurate data as possible. The goal of this document is to identify procedures that ensure the implementation of this policy.

B. Quality Assurance Objectives

Quality assurance objectives for pesticide monitoring are: (1) to establish the necessary quality control activities relating to site selection, sample collection, sampling protocol, sample analysis, data reduction and validation, and final reports; and (2) to assess data quality in terms of precision, accuracy and completeness.

II. Siting

Probe siting criteria for ambient pesticide monitoring are listed in TABLE 1. Normally four sites will be chosen. The monitoring objective for these sites is to measure population exposure near the perimeter of towns or in the area of the town where the highest concentrations are expected based on prevailing winds and proximity to applications. One of these sites is usually designated to be an urban area "background" site and is located away from any expected applications; however, because application sites are not known prior to the start of monitoring, a "zero level" background may not occur. Detectable levels of some pesticides may also be found at an urban area background site if they are marketed for residential as well as commercial use.

Probe siting criteria for placement of samplers near a pesticide application for collection of samples are the same as ambient monitoring (TABLE 1). In addition, the placement of the application samplers should be to obtain upwind and downwind concentrations of the pesticide. Since winds are variable and do not always conform to expected patterns, the goal is to surround the

application field with one sampler on each side (assuming the normal rectangular shape) at a distance of about 20 yards from the perimeter of the field. However, conditions at the site will dictate the actual placement of monitoring stations. Once monitoring has begun, the sampling stations will not be moved, even if the wind direction has changed.

III. Sampling

All sampling will be coordinated through the County Agricultural Commissioner's Office and the local Air Quality Management District (AQMD) or Air Pollution Control District (APCD). Monitoring sites will be arranged through the cooperation of applicators, growers or owners for application monitoring. For selection of ambient sites, ARB staff will work through authorized representatives of private companies or government agencies.

A. Background Sampling

A background sample will be taken at all sites prior to an application. It should be a minimum of one hour and longer if scheduling permits. This sample will establish if any of the pesticide being monitored is present prior to the application. It also can indicate if other environmental factors are interfering with the detection of the pesticide of concern during analysis.

While one of the sampling sites for ambient monitoring is referred to as an "urban area background," it is not a background sample in the conventional sense because the intent is not to find a non-detectable level or a "background" level prior to a particular event (or application). This site is chosen to represent a low probability of finding the pesticide and a high probability of public exposure if significant levels of the pesticide are detected at this urban background site.

B. Schedule

Samples for ambient pesticide monitoring will be collected over 24-hour periods on a schedule, in general, of 4 samples per week for 4 weeks. Field application monitoring will follow the schedule guidelines outlined in TABLE 2.

C. Blanks and Spikes

Field blanks should be included with each batch of samples submitted for analysis. This will usually require one blank for an application monitoring and one blank per week for an ambient monitoring program. Whenever possible, trip spikes should be provided for both ambient and application monitoring. The spiked samples should be stored in the same manner as the samples and returned to the laboratory for analysis.

D. Meteorological Station

Data on wind speed and direction will be collected during application monitoring by use of an on-site meteorological station. If appropriate

equipment is available, temperature and humidity data should also be collected and all meteorological data recorded on a data logger. Meteorological data are not collected for ambient monitoring.

E. Collocation

For both ambient and application monitoring, precision will be demonstrated by collecting samples from a collocated sampling site. An additional ambient sampler will be collocated with one of the samplers and will be rotated among the sampling sites so that duplicate samples are collected at at least three different sites. The samplers should be located between two and four meters apart if they are high volume samplers in order to preclude airflow interference. This consideration is not necessary for low (<20 liters/min.) flow samplers. The duplicate sampler for application monitoring should be downwind at the sampling site where the highest concentrations are expected. When feasible, duplicate application samples should be collected at every site.

F. Calibration

Field flow calibrators (rotometers, flow meters or critical orifices) shall be calibrated against a referenced standard prior to a monitoring period. This referenced standard should be verified, certified or calibrated with respect to a primary standard at least once a year with the method clearly documented. Sampling flow rates should be checked in the field and noted before and after each sampling period. Before flow rates are checked, the sampling system should be leak checked.

G. Flow Audit

A flow audit of the field air samplers should be conducted by an independent agency prior to monitoring. If results of this audit indicate actual flow rates differ from the calibrated values by more than 10%, the field calibrators should be rechecked until they meet this objective.

H. Log Sheets

Field data sheets will be used to record sampling date and location, initials of individuals conducting sampling, sample number or identification, initial and final time, initial and final flow rate, malfunctions, leak checks, weather conditions (e.g., rain) and any other pertinent data which could influence sample results.

I. Preventative Maintenance

To prevent loss of data, spare pumps and other sampling materials should be kept available in the field by the operator. A periodic check of sampling pumps, meteorological instruments, extension cords, etc., should be made by sampling personnel.

TABLE 1. PESTICIDE PROBE SITING CRITERIA SUMMARY

The following probe siting criteria apply to pesticide monitoring and are summarized from the U.S. EPA ambient monitoring criteria (40 CFR 58) which are used by the ARB.

Height Above Ground (Meters)	Minimum Distance From Supporting Structure (Meters)		Other Spacing Criteria
	Vertical	Horizontal	
2-15	1	1	1. Should be 20 meters from trees. 2. Distance from sampler to obstacle, such as buildings, must be at least twice the height the obstacle protrudes above the sampler. 3. Must have unrestricted air-flow 270° around sampler. 4. Samplers at a collocated site (duplicate for quality assurance) should be 2-4 meters apart if samplers are high flow, >20 liters per minute.

TABLE 2. GUIDELINES FOR APPLICATION SAMPLING SCHEDULE

All samplers should be sited approximately 20 yards from the edge of the field; four samplers to surround the field whenever possible. At least one site should have a collocated (duplicate) sampler.

The approximate sampling schedule for each station is listed below; however, these are only approximate guidelines since starting time and length of application will dictate variances.

- Background sample (minimum 1-hour sample: within 24 hours prior to application).
- Application + 1 hour after application combined sample.
- 2-hour sample from 1 to 3 hours after the application.
- 4-hour sample from 3 to 7 hours after the application.
- 8-hour sample from 7 to 15 hours after the application.
- 9-hour sample from 15 to 24 hours after the application.
- 1st 24-hour sample starting at the end of the 9-hour sample.
- 2nd 24-hour sample starting 24 hours after the end of the 9-hour sample.

IV. Protocol

Prior to conducting any pesticide monitoring, a protocol, using this document as a guideline, will be written by the ARB staff. The protocol describes the overall monitoring program, the purpose of the monitoring and includes the following topics:

1. Identification of the sample site locations, if possible.

2. Description of the sampling train and a schematic showing the component parts and their relationship to one another in the assembled train, including specifics of the sampling media (e.g., resin type and volume, filter composition, pore size and diameter, catalog number, etc.).

3. Specification of sampling periods and flow rates.

4. Description of the analytical method.

5. Tentative test schedule and expected test personnel.

Specific sampling methods and activities will also be described in the monitoring plan (protocol) for review by ARB and DPR. Criteria which apply to all sampling include: (1) chain of custody forms (APPENDIX I), accompanying all samples, (2) light and rain shields protecting samples during monitoring, and (3) storing samples in an ice chest (with dry ice if required for sample stability) or freezer, until delivery to the laboratory. The protocol should include: equipment specifications (when necessary), special sample handling and an outline of sampling procedures. The protocol should specify any procedures unique to a specific pesticide.

V. Analysis

Analysis of all field samples must be conducted by a fully competent laboratory. To ensure the capability of the laboratory, an analytical audit and systems audit should be performed by the ARB Quality Management and Operations Support Branch (QMOSB) prior to the first analysis. After a history of competence is demonstrated, an audit prior to each analysis is not necessary. However, during each analysis spiked samples should be provided to the laboratory to demonstrate accuracy.

A. Standard Operating Procedures

Analysis methods should be documented in a Standard Operating Procedure (S.O.P.) before monitoring begins. The S.O.P. includes: instrument and operating parameters, sample preparation, calibration procedures and quality assurance procedures. The limit of quantitation must be defined if different than the limit of detection. The method of calculating these values should also be clearly explained in the S.O.P.

1. Instrument and Operating Parameters

   A complete description of the instrument and the conditions should be given so that any qualified person could duplicate the analysis.

2. Sample Preparation

   Detailed information should be given for sample preparation including equipment and solvents required.

3. Calibration Procedures

   The S.O.P. plan will specify calibration procedures including intervals for recalibration, calibration standards, environmental conditions for calibrations and a calibration record keeping system. When possible, National Institute of Standards and Technology traceable standards should be used for calibration of the analytical instruments in accordance with standard analytical procedures which include multiple calibration points that bracket the expected concentrations.

4. Quality Control

   Validation testing should provide an assessment of accuracy, precision, interferences, method recovery, analysis of pertinent breakdown products and limits of detection (and quantitation if different from the limit of detection). Method documentation should include confirmation testing with another method when possible, and quality control activities necessary to routinely monitor data quality control such as use of control samples, control charts, use of surrogates to verify individual sample recovery, field blanks, lab blanks and duplicate analysis. All data should be properly recorded in a laboratory notebook.

   The method should include the frequency of analysis for quality control samples. Analysis of quality control samples are recommended before each day of laboratory analysis and after every tenth sample. Control samples should be found to be within control limits previously established by the lab performing the analysis. If results are outside the control limits, the method should be reviewed, the instrument recalibrated and the control sample reanalyzed.

   All quality control studies should be completed prior to sampling and include recovery data from at least three samples spiked at least two concentrations. Instrument variability should be assessed with three replicate injections of a single sample at each of the spiked concentrations. A stability study should be done with triplicate spiked samples being stored under actual conditions and analyzed at appropriate time intervals. This study should be conducted for a minimum period of time equal to the anticipated storage period. Prior to each sampling study, a conversion/collection efficiency study should be conducted under field conditions (drawing ambient air through spiked sample media at actual flow rates for the recommended sampling time) with three

replicates at two spiked concentrations and a blank. Breakthrough studies should also be conducted to determine the capacity of the adsorbent material if high levels of pesticide are expected or if the suitability of the adsorbent is uncertain.

VI. Final Reports and Data Reduction

The mass of pesticide found in each sample should be used along with the volume of air sampled (from the field data sheet) to calculate the mass per volume for each sample. For each sampling date and site, concentrations should be reported in a table as ug/m^3 (microgram per cubic meter). When the pesticide exists in the vapor phase under ambient conditions, the concentration should also be reported as ppbv (parts per billion, by volume) or the appropriate volume-to-volume units. Collocated samples should be reported separately as raw data, but then averaged and treated as a single sample for any data summaries. For samples where the end flow rate is different from that set at the start of the sampling period, the average of these two flow rates should be used to determine the total sample volume; however, the minimum and maximum concentrations possible for that sample should also be presented.

The final report should indicate the dates of sampling as well as the dates of analyses. These data can be compared with the stability studies to determine if degradation of the samples has occurred.

Final reports of all monitoring are sent to the Department of Pesticide Regulation, the Agricultural Commissioner's Office, the local AQMD as well as the applicator and/or the grower. Final reports are available to the public by contacting the ARB Engineering Evaluation Branch.

A. Ambient Reports

The final report for ambient monitoring should include a map of the monitored area which shows nearby towns or communities and their relationship to the monitoring stations, along with a list of the monitoring locations (e.g., name and address of the business or public building). A site description should be completed for any monitoring site which might have characteristics that could affect the monitoring results (e.g., obstructions). For ambient monitoring reports, information on terrain, obstructions and other physical properties which do not conform to the siting criteria or may influence the data should be described.

Ambient data should be summarized for each monitoring location by maximum and second maximum concentration, average (using only those values greater than the minimum quantitation limit), total number of samples and number of samples above the minimum quantitation limit. For this purpose, collocated samples are averaged and treated as a single sample.

B. Application Reports

Similarly, a map or sketch indicating the general location (nearby towns, highways, etc.) of the field chosen for application monitoring should be included as well as a detailed drawing of the field itself and the relative positions of the monitors. For application monitoring reports, as

much data as possible should be collected about the application conditions (e.g., formulation, application rate, acreage applied, length of application and method of application). This may be provided either through a copy of the Notice of Intent, the Pesticide Control Advisor's (PCA) recommendation or completion of the Application Site Checklist (APPENDIX II). Wind speed and direction data should be reported for the application site during the monitoring period. Any additional meteorological data collected should also be reported.

C. Quality Assurance

All quality control and quality assurance samples (blanks, spikes, etc.) analyzed by the laboratory must be reported. Results of all method development and/or validation studies (if not contained in the S.O.P.) will also be reported. The results of any quality assurance activities conducted by an agency other than the analytical laboratory should be included in the report as an appendix. This includes analytical audits, system audits and flow rate audits.

CALIFORNIA AIR RESOURCES BOARD
MONITORING & LABORATORY DIVISION
P.O. Box 2815, Sacramento CA 95812

CHAIN OF CUSTODY

SAMPLE RECORD

Job #: _____ Date: ____/____/____
Sample/Run #: _____ Time: _____
Job name: _____
Sample Location: _____
Type of Sample: _____
Log #'s: _____

ACTION	DATE	TIME	INITIALS		METHOD OF STORAGE freezer, ice or dry ice
Sample Collected			GIVEN BY	TAKEN BY	
Transfer					
Transfer					
Transfer					
Transfer					
Transfer					
Transfer					

LOG #	ID #	DESCRIPTION

RETURN THIS FORM TO: _____

APPLICATION CHECKLIST

1. Field size.
2. Field location (Section, Range and Township).
3. Application rate.
4. Formulation.
5. Method of application (ground, air, irrigation, injection, tarping after application, etc.)
6. Length of application.
7. Any unusual weather conditions during application or monitoring period (rain, fog, wind).
8. Any visible drift from the field?
9. Pattern of application (e.g., east to west).

APPENDIX IV.

CIMIS WEATHER DATA

Hourly weather data for Station 8 Delano

DATE	HOUR	RAIN	HYPER PARCIP	EXPER SOLAR	NET	VAPOR PRESSURE	AIR TEMP	RELATIVE HUMIDITY	DEW-POINT	WIND SPEED	WIND DIR	REF
			#1	#2								
		in.	in.	---Ly/day---		mBars	F	%	F	mph	(0-360)	
7/28/94	1	0.00	0.00	-1	-68	19.42	67.2	85	62.7	1.8	314	
13.3		81.8	85.30	85.30								
	2	0.00	0.00	-1	-70	17.75	66.3	80	60.1	1.5	190	
60.8		81.0	80.50	80.50								
	3	0.00	0.00	-1	-69	17.31	63.5	86	59.4	1.3	106	
70.5		80.2	86.50	86.50								
	4	0.00	0.00	-1	-69	17.05	61.7	91	59.0	1.5	19	
45.9		79.4	90.70	90.70								
	5	0.00	0.00	0	-68	16.95	60.5	94	58.8	1.3	65	
62.7		78.7	94.30	94.30								
	6	0.00	0.00	118	7	16.98	61.4	91	58.9	1.7	119	
38.2		77.9	91.40	91.40								
	7	0.00	0.00	394	221	17.94	65.6	83	60.4	3.5	122	
11.6		77.3	83.60	83.60								
	8	0.01	0.00	802	461	17.71	69.3	72	60.1	3.4	134	
19.8		76.9	72.40	72.40								
	9	0.02	0.00	1174	703	18.09	74.2	63	60.7	3.1	121	
27.7		76.8	62.76	62.76								
	10	0.02	0.00	1534	933	17.80	77.6	55	60.2	5.1	138	
19.4		77.2	55.05	55.05								
	11	0.03	0.00	1759	1088	18.78	80.6	53	61.7	6.2	149	
24.5		78.2	52.66	52.66								
	12	0.03	0.00	1852	1171	19.44	83.2	50	62.7	6.3	143	
20.5		79.7	50.06	50.06								
	13	0.03	0.00	1904	1195	19.28	86.1	45	62.5	6.2	146	
21.2		81.5	45.28	45.28								
	14	0.03	0.00	1797	1129	18.61	88.2	41	61.5	6.7	141	
16.5		83.4	40.96	40.96								
	15	0.03	0.00	1617	998	16.51	90.0	34	58.1	6.5	155	
18.1		85.1	34.33	34.33								
	16	0.02	0.00	1318	796	16.67	91.0	34	58.4	7.4	157	
18.4		86.6	33.55	33.55								
	17	0.02	0.00	952	551	15.30	91.7	30	56.0	6.5	143	
15.5		87.6	30.17	30.17								
	18	0.01	0.00	536	298	16.73	90.6	34	58.5	5.4	141	
17.2		88.1	34.37	34.37								
	19	0.00	0.00	198	57	19.91	86.4	46	63.4	3.6	136	
12.0		88.2	46.31	46.31								
	20	0.00	0.00	9	-66	19.66	81.8	53	63.0	2.6	158	
22.5		87.7	53.05	53.05								
	21	0.00	0.00	-1	-71	19.13	76.6	61	62.2	1.6	199	
53.3		87.0	61.26	61.26								
	22	0.00	0.00	-1	-71	18.79	73.6	67	61.7	1.6	66	
16.0		86.1	66.51	66.51								
	23	0.00	0.00	-1	-69	19.43	70.7	76	62.7	2.6	77	
16.7		85.1	75.90	75.90								

	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]	[illegible]			[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]									
	2	[illegible]	[illegible]	-1	[illegible]	17.[illegible]	64.3	8[illegible]	[illegible]	1.7	30[illegible]	
[illegible]	87.[illegible]	84.7[illegible]	8[illegible]									
	3	[illegible]	0.00	-1	-7[illegible]	1[illegible].55	63.1	89	[illegible]	1.5	34[illegible]	[illegible]
59.0	[illegible]1.4	89.10	89.10									
	4	[illegible]	0.00	-1	-73	17.40	61.9	92	59.6	1.3	0	
[illegible].8	80.[illegible]	92.00	92.00									
	5	[illegible]	0.00	0	-78	16.74	60.4	93	58.5	1.3	51	[illegible]
[illegible]	79.[illegible]	93.20	93.20									
	6	0.00	0.00	62	-29	16.90	60.4	94	58.7	1.5	310	[illegible]
44.0	79.1	94.40	94.40									
	7	0.00	0.00	419	231	17.21	64.1	84	59.3	3.4	143	2
17.0	78.4	84.40	84.40									
	8	0.01	0.00	855	482	16.86	68.5	71	58.7	3.0	125	3
23.4	77.9	70.90	70.90									
	9	0.02	0.00	1199	713	17.28	74.1	60	59.4	2.6	106	2
38.0	77.8	60.06	60.06									
	10	0.02	0.00	1510	926	18.26	78.0	56	60.9	4.7	126	4
22.6	78.2	55.71	55.71									
	11	0.03	0.00	1726	1079	18.23	81.1	50	60.9	5.2	132	4
20.4	79.3	50.33	50.33									
	12	0.03	0.00	1943	1189	18.43	83.8	47	61.2	5.3	140	4
27.0	80.8	46.58	46.58									
	13	0.03	0.00	1588	1002	18.24	85.3	44	60.9	5.8	139	5
28.4	82.7	43.97	43.97									
	14	0.03	0.00	1875	1135	18.27	87.9	40	60.9	6.9	146	6
16.7	84.5	40.49	40.49									
	15	0.03	0.00	1627	1008	19.87	89.0	43	63.3	7.2	134	7
11.5	86.1	42.53	42.53									
	16	0.02	0.00	1173	711	18.62	89.7	39	61.5	7.1	160	6
18.9	87.6	39.07	39.07									
	17	0.02	0.00	764	442	18.00	89.5	38	60.5	7.9	163	7
15.2	88.5	38.05	38.05									
	18	0.01	0.00	432	242	19.19	88.4	42	62.3	6.2	166	6
13.0	89.0	41.91	41.91									
	19	0.00	0.00	169	53	20.25	85.2	49	63.9	4.4	151	4
13.0	88.8	48.93	48.93									
	20	0.00	0.00	10	-51	19.62	79.9	56	63.0	2.9	131	2
15.5	88.2	56.60	56.60									
	21	0.00	0.00	-1	-55	20.42	73.6	72	64.1	1.5	108	1
11.6	87.5	72.10	72.10									
	22	0.00	0.00	-1	-55	20.68	71.7	78	64.5	1.6	332	0
39.3	86.6	78.10	78.10									
	23	0.00	0.00	-1	-55	19.83	70.5	78	63.3	2.9	40	1
29.4	85.6	77.80	77.80									
	24	0.00	0.00	-1	-57	17.84	68.7	75	60.3	2.5	142	1
59.1	84.6	74.60	74.60									

7/29/94 0.24 = TOTAL ETo

1 calorie/sq.cm/day (Ly/day)*.484=W/sq.m inches*25.4=mm (F-32)*5/9=C

mph*.447=m/s mBars*.1=kPa

------------------------------ SEVERE FLAGS ------------------------------

INFORMATIVE FLAGS --------------------

N/C -not collected N/A -not available noc -cannot calculate Y -out of range

-all quality control not performed

S -not in service R -out of range I -ignore,no meaning F -estimated

* * * * PRELIMINARY DATA * * * * note: TOTAL ETo = sum

of hourly ET

Date	Hr									SPEED	DIR				
							F	%	F	mph	(0-360)				
[illegible]	1	0.00	0.00	-1	-74	17.60	66.3	80	59.9	1.9	16	[illegible]	81.6	79.90	79.90
	2	0.00	0.00	-1	-75	16.33	63.5	82	57.8	2.5	108	10.5	82.7	81.80	81.80
	3	0.00	0.00	-1	-74	16.76	63.1	85	58.5	2.9	180	47.6	81.9	85.00	85.00
	4	0.00	0.00	-1	-73	16.78	61.1	91	58.5	2.2	29	58.8	81.1	91.20	91.20
	5	0.00	0.00	0	-74	16.04	59.8	92	57.3	2.3	37	27.7	80.3	91.60	91.60
	6	0.00	0.00	94	-15	15.85	60.0	90	57.0	1.7	149	58.2	79.5	89.60	89.60
	7	0.00	0.00	408	224	15.93	64.2	78	57.1	3.5	181	26.1	78.9	77.80	77.80
	8	0.01	0.00	790	451	15.97	67.0	71	57.2	3.8	137	23.0	78.4	70.80	70.80
	9	0.02	0.00	1171	698	16.49	71.1	64	58.1	3.8	114	26.3	78.2	63.54	63.54
	10	0.02	0.00	1493	918	17.58	74.9	60	59.9	4.5	131	28.3	78.5	59.60	59.60
	11	0.03	0.00	1733	1081	18.12	79.1	53	60.7	5.5	132	21.7	79.5	53.44	53.44
	12	0.03	0.00	1867	1172	18.50	81.9	50	61.3	6.1	133	18.0	81.0	49.77	49.77
	13	0.03	0.00	1906	1192	19.72	84.4	49	63.1	6.5	135	20.6	82.9	48.93	48.93
	14	0.03	0.00	1821	1137	19.52	86.1	46	62.8	7.3	143	19.7	84.8	45.85	45.85
	15	0.03	0.00	1619	1006	21.38	87.1	49	65.4	8.4	146	15.5	86.5	48.67	48.67
	16	0.02	0.00	1325	803	19.94	87.8	44	63.4	8.8	162	15.9	88.0	44.42	44.42
	17	0.02	0.00	965	563	19.81	87.9	44	63.2	8.9	156	14.9	88.9	43.93	43.93
	18	0.01	0.00	566	316	19.95	86.8	46	63.4	8.9	166	12.1	89.4	45.80	45.80
	19	0.00	0.00	199	52	20.62	83.9	52	64.4	5.4	162	14.5	89.3	52.08	52.08
	20	0.00	0.00	7	-72	20.39	78.4	61	64.1	6.2	174	15.8	88.7	61.51	61.51
	21	0.00	0.00	-1	-76	19.06	72.1	71	62.1	3.1	174	24.6	87.9	71.00	71.00
	22	0.00	0.00	-1	-75	18.31	67.5	80	61.0	2.4	155	41.3	86.8	79.70	79.70
	23	0.00	0.00	-1	-76	17.11	65.2	80	59.1	1.9	175	53.9	85.6	80.60	80.60
	24	0.00	0.00	-1	-75	16.94	62.8	87	58.8	1.7	173	72.3	84.5	87.00	87.00
7/30/94		0.24 = TOTAL ETo													
7/31/94	1	0.00	0.00	-1	-77	15.62	61.9	83	56.6	2.9	116	17.0	83.4	82.60	82.60
	2	0.00	0.00	-1	-77	15.31	60.3	86	56.0	3.1	158	47.2	82.4	85.60	85.60
	3	0.00	0.00	-1	-77	15.11	59.0	88	55.6	2.7	218	25.4	81.5	88.40	88.40

HOUR	ETo	PRECIP	SOLAR	NET	PRESSURE	TEMP	HUMIDITY	DEW POINT	WIND SPEED	WIND DIR	RES	STD.DEV. WIND DIR	SOIL TEMP	EXPER #1	EXPER #2
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	15.14	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	91.70
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	56.5	4.1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	78.50
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	16.04	67.5	[illegible]	57.3	3.1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	69.78
10	[illegible]	0.00	1483	912	16.37	72.2	62	59.7	4.4	141	[illegible]	[illegible]	77.9	62.47	62.47
11	0.02	0.00	1728	1078	17.29	75.9	57	59.4	4.3	142	3	39.9	78.9	56.69	56.69
12	0.03	0.00	1863	1171	17.95	78.5	54	60.4	5.4	138	[illegible]	24.0	80.4	53.92	53.92
13	0.03	0.00	1892	1189	18.24	80.7	51	60.9	6.6	136	6	19.3	82.3	51.01	51.01
14	0.03	0.00	1815	1134	18.51	82.3	49	61.3	7.4	141	7	16.9	84.3	49.14	49.14
15	0.03	0.00	1617	1002	19.26	83.6	49	62.4	7.6	146	7	20.4	86.0	48.97	48.97
16	0.02	0.00	1322	802	19.78	84.3	49	63.2	7.1	146	6	24.3	87.4	49.19	49.19
17	0.02	0.00	954	558	20.34	84.3	51	64.0	6.8	148	6	22.0	88.4	50.56	50.56
18	0.01	0.00	550	308	20.49	83.6	52	64.2	5.5	140	5	14.2	88.9	52.07	52.07
19	0.00	0.00	152	38	20.33	79.5	59	64.0	4.1	136	4	8.2	88.9	59.03	59.03
20	0.00	0.00	7	-70	18.56	74.7	63	61.4	3.5	145	3	15.6	88.4	63.20	63.20
21	0.00	0.00	-1	-77	17.10	72.3	63	59.1	3.1	176	3	23.2	87.5	63.28	63.28
22	0.00	0.00	-1	-74	17.13	67.0	76	59.1	1.9	115	1	50.2	86.5	76.00	76.00
23	0.00	0.00	-1	-75	16.15	64.5	78	57.5	3.0	125	[illegible]	16.4	85.4	77.90	77.90
24	0.00	0.00	-1	-74	15.44	61.6	82	56.2	1.6	105	1	13.6	84.4	82.50	82.50

7/31/94 0.23 = TOTAL ETo

1 calorie/sq.cm/day (Ly/day)*.484=W/sq.m inches*25.4=mm (F-32)*5/9=C
mph*.447=m/s mBars*.1=kPa

------------------------------ SEVERE FLAGS ------------------------------

INFORMATIVE FLAGS --------------------

N/C -not collected N/A -not available noc -cannot calculate Y -out of range
--!! quality control not performed
S -not in service R -out of range I -ignore,no meaning F -estimated
* * * * PRELIMINARY DATA * * * * note: TOTAL ETo = sum of hourly ET

California Irrigation Management Information System - Department of Water Resources

Hourly Weather Data for Station # 61 Orland

			RADIATION		VAPOR	AIR	RELATIVE	DEW-	WIND	WIND	RES
STD.DEV.	SOIL	EXPER	EXPER								
DATE	HOUR	ETo	PRECIP	SOLAR	NET	PRESSURE	TEMP	HUMIDITY	POINT	SPEED	DIR
WIND DIR	TEMP	#1	#2								
		in.	in.	---Ly/day---		mBars	F	%	F	mph	(0-360)
	F										

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]		[illegible]		
[illegible]	[illegible]	[illegible]	[illegible]							
[illegible]	[illegible]	[illegible]	-1	[illegible]	[illegible]	56.8	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	90.40							
4	[illegible]	[illegible]	-2	-46	[illegible]	55.8	[illegible]	54.6	1.7	349
[illegible]	[illegible]	[illegible]	95.50							
5	[illegible]	[illegible]	-1	-52	[illegible]	55.4	[illegible]	54.2	2.6	30
[illegible]	[illegible]	[illegible]	93.60							
6	[illegible]	0.00	92	-23	14.55	56.1	83	54.6	2.3	102
[illegible]	78.8	94.50	94.60							
7	0.00	0.00	427	230	13.42	59.5	89	56.2	3.5	175
[illegible]	78.1	88.90	88.90							
8	0.01	0.00	794	452	15.53	62.7	80	56.4	3.5	167
36.8	77.6	80.00	80.00							
9	0.01	0.00	1169	697	16.29	66.5	73	57.7	5.1	124
25.1	77.4	73.50	73.50							
10	0.02	0.00	1501	919	16.89	70.7	66	58.7	5.0	152
30.9	77.8	65.97	65.97							
11	0.02	0.00	1757	1055	17.30	73.7	61	59.4	5.7	155
29.6	78.7	61.03	61.03							
12	0.03	0.00	1900	1156	17.22	77.5	53	59.3	4.7	120
34.3	80.2	53.43	53.43							
13	0.03	0.00	1920	1172	18.34	79.6	53	61.0	5.9	156
26.5	82.1	53.15	53.15							
14	0.03	0.00	1834	1107	18.54	81.8	50	61.3	6.7	147
20.2	84.1	50.07	50.07							
15	0.03	0.00	1633	1005	18.70	84.1	47	61.6	7.7	149
14.2	85.9	46.89	46.89							
16	0.02	0.00	1332	804	19.10	84.9	47	62.2	8.0	139
13.1	87.4	46.59	46.59							
17	0.02	0.00	974	563	17.06	85.2	41	59.0	8.0	159
20.4	88.4	41.31	41.31							
18	0.01	0.00	553	307	19.61	84.1	49	62.9	7.6	153
16.4	88.9	49.19	49.19							
19	0.00	0.00	174	36	19.01	80.9	53	62.1	4.0	152
18.5	88.8	52.76	52.76							
20	0.00	0.00	7	-70	19.73	74.9	67	63.1	2.1	129
17.1	88.2	66.99	66.99							
21	0.00	0.00	-1	-73	20.24	70.1	80	63.8	1.4	125
65.7	87.4	80.50	80.50							
22	0.00	0.00	-1	-72	19.97	68.1	85	63.5	1.5	285
48.4	86.4	85.20	85.20							
23	0.00	0.00	-1	-73	18.69	66.5	84	61.6	2.8	55
13.2	85.3	84.30	84.30							
24	0.00	0.00	-1	-74	17.40	64.5	84	59.6	2.9	101
12.6	84.3	84.00	84.00							

8/ 1/94 0.22 = TOTAL ETo

1 calorie/sq.cm/day (Ly/day)*.484=W/sq.m inches*25.4=mm (F-32)*5/9=C

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* * * PRELIMINARY DATA * * * * note: TOTAL ETo = su

* hourly ET

APPENDIX V.

QMOSB AUDIT REPORT

STATE OF CALIFORNIA
AIR RESOURCES BOARD
2020 L STREET
P.O. BOX 2815
SACRAMENTO, CA 95812

PETE WILSON, Governor

MEMORANDUM

TO: George Lew, Chief
Engineering and Laboratory Branch

THROUGH: Jeff Cook, Chief
Quality Management and Operations Support Branch

FROM: Alice Westerinen, Manager
Quality Assurance Section

DATE: February 21, 1995

SUBJECT: Azinphos Methyl Monitoring Audit Report

Attached is the final quality assurance audit report on the azinphos methyl monitoring project conducted in August of 1994 by the Engineering Evaluation Branch of the Air Resources Board.

If you have any questions, please contact Ms. Jane Pettit of my staff at (916) 322-7317.

Attachment

cc: Don Fitzell
Jane Pettit

STATE OF CALIFORNIA

AIR RESOURCES BOARD

AUDIT REPORT

AZINPHOS METHYL MONITORING IN GLENN COUNTY

MONITORING AND LABORATORY DIVISION

QUALITY ASSURANCE SECTION

FEBRUARY 21, 1995

AUDIT REPORT

AZINPHOS METHYL MONITORING IN GLENN COUNTY

TABLE OF CONTENTS

ATTACHMENTS

I. EXECUTIVE SUMMARY

In August of 1994, the Engineering Evaluation Branch of the California Air Resources Board (CARB) conducted ambient air sampling in Glenn County, California, to document the airborne emissions of azinphos methyl in the vicinity of a treated field during and after an application. The samples were analyzed by the Engineering Evaluation Branch laboratory.

The Monitoring and Laboratory Division's Quality Assurance Section staff conducted a system audit of the field and laboratory operations to review the sample handling and storage procedures, analytical methodology, and method validation. It was found that laboratory practices were consistent with the Quality Assurance Plan for Pesticide Monitoring (CARB, February 4, 1994).

Quality Assurance Section staff conducted a flow rate audit of the air samplers used in the monitoring. The difference between the reported and true flow rates averaged 0.46% with a range of -3.14% to 1.65%.

Seven samples spiked with measured amounts of azinphos methyl were submitted to the laboratory for analysis. The samples were prepared from azinphos methyl standards obtained from Chem Service. The difference between the assigned and the reported total mass averaged -32% with a range of -35% to -27%.

II. CONCLUSIONS

The records for field operations, sample handling and storage procedures, analytical methodology, and method validation were in agreement with the Quality Assurance Plan for Pesticide Monitoring. The results of the reported flow rates were in good agreement with the actual flow rates measured by Quality Assurance Section staff. The results of the analytical performance audit showed a negative bias averaging -32%. The cause of this bias is unclear, and may be related to the preparation of the audit samples or to the analytical method.

III. RECOMMENDATIONS

In the future, the Quality Assurance Section will attempt to obtain samples which are already in solution. This will allow Quality Assurance Section staff to spike the audit samples with a spiking solution certified by the vendor. This should eliminate the potential for dilution errors.

IV. INTRODUCTION

In August of 1994, the Engineering Evaluation Branch (EEB) of the California Air Resources Board (CARB) conducted ambient air sampling in Glenn County, California, to document the airborne emissions of azinphos methyl in the vicinity of a treated field during and after an application. The samples were analyzed by the EEB laboratory. Monitoring and Laboratory Division (MLD) Quality Assurance Section (QAS) staff conducted a system audit of the field and laboratory operations, and performance audits of the air samplers and the analytical method.

V. AUDIT OBJECTIVE

The system audit was conducted to determine whether the quality control practices followed in the handling and storage of samples, analytical methodology, and method validation were consistent with the Quality Assurance Plan for Pesticide Monitoring (CARB, February 4, 1994). Performance audits were conducted to evaluate the accuracy of the air samplers' flow rate and the analytical method.

VI. FIELD AND LABORATORY OPERATIONS

A system audit of the field and laboratory operations was initiated in September 1994 through a questionnaire submitted to EEB staff. Also, the protocol for ambient air monitoring of azinphos methyl and the laboratory standard operating procedure for the analysis of azinphos methyl were reviewed. The following is a discussion of the audit findings.

Sample Handling and Storage

Samples were collected by drawing ambient air at measured rates through glass tubes containing 600 mg of XAD-2 adsorbent resin. The air samplers consisted of two sampling tubes, each connected with Teflon tubing to an in-line rotameter, which in turn was connected to an air pump. The sampling assembly was supported by a two meter section of galvanized steel tube (Figure 1). The samplers' rotameters were set to an indicated flow rate of 2.0 liters per minute (LPM) by adjusting the control valve on the rotameter.

Sampling was conducted following the schedule specified in the sampling protocol. After sampling, the exposed XAD-2 tubes were collected, capped, and placed in screw-cap glass culture tubes. The tubes were then stored over ice in an ice chest until they were delivered to the laboratory at the end of the three-day sampling period.

Upon receipt at the laboratory, the samples were stored in a freezer for less than a week before extraction and analyses were conducted.

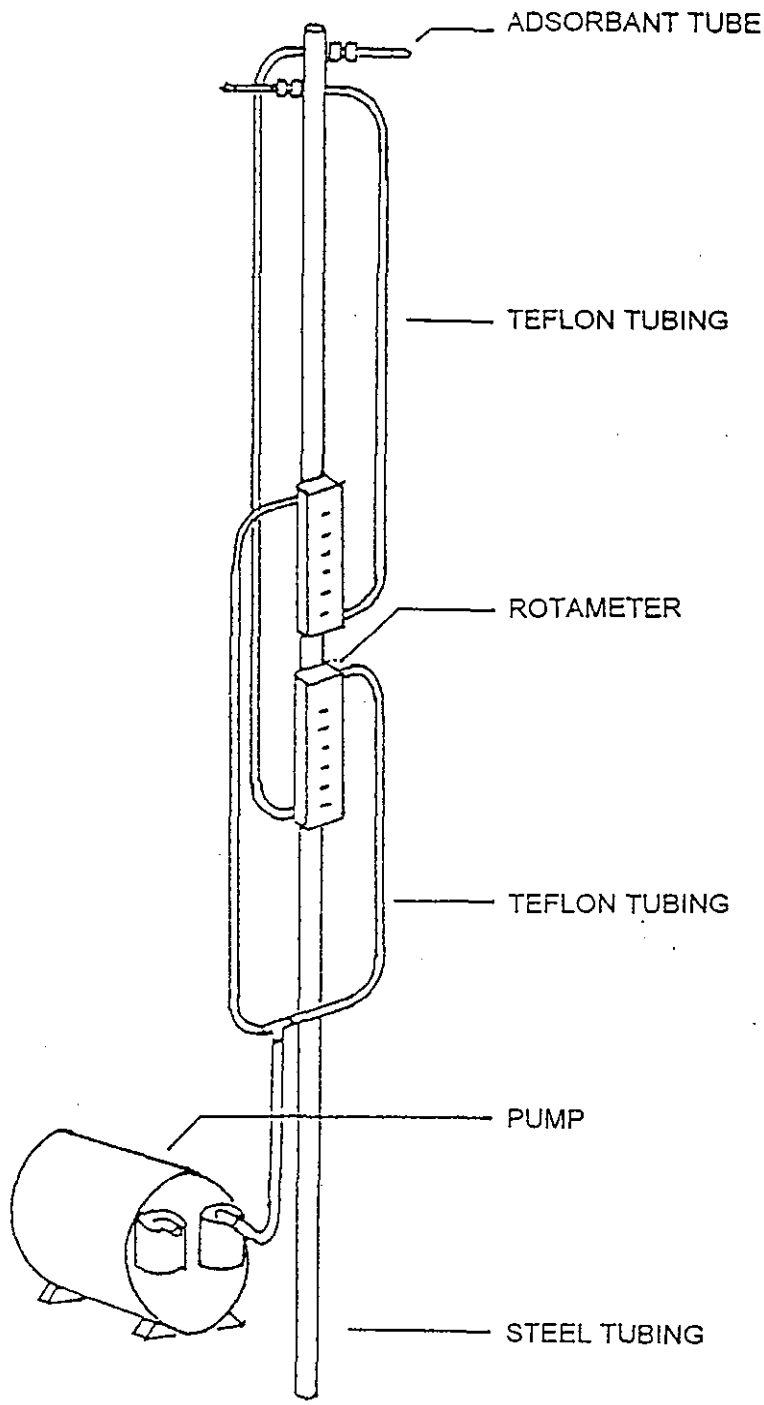

Figure 1. Air sampler used in the monitoring of azinphos methyl

Sample Analysis

The analytical method was developed by the Northern Laboratory Branch of MLD, and is described in a document entitled "Standard Operating Procedure for the Determination of Azinphos Methyl in Ambient Air (Preliminary Draft 1, July 1, 1987)". The method entails extraction of the sampling tubes with an 80/20 isooctane/acetone mixture and analysis by Gas Chromatography (GC). The analyses were performed with a Varian 3400 GC with a Nitrogen-Phosphorus detector.

The chromatograph was calibrated before each analytical run. Calibration standards of 0.025, 0.05, 0.1, and 1.0 ug/ml were prepared just before analyses from a neat azinphos methyl sample obtained from Chem Service. The standards were stored in a freezer, and were determined to be stable for over one month.

Quality control activities performed to monitor and document the quality of the data included analysis of a laboratory spike and 3 field spikes; analysis of a method blank; one field blank per shipment of samples; and analysis of duplicate samples from collocated samplers at two of four sites. Control samples consisted of single point calibrations taken at the beginning, middle, and end of the sample analysis period. These calibration points gave one calibration curve.

Method Validation

The limit of detection (LOD) was defined as the intercept of the calibration curve plus three standard deviations. The LOD was calculated as 0.07 ug per sample. Trapping efficiency was determined as 86% to 88%. Stability studies were conducted for samples stored at -4 ^{o}C. After 10 days, the recovery ranged from 87% to 92%.

Documentation

All the samples received at the laboratory were accompanied by chain-of-custody records. Field data sheets containing the sample collection information were retained by EEB staff. The information recorded in the field data sheets included sampler location, sampling date, start and stop times, initial and final flow rates, and comments about unusual conditions.

Laboratory and instrument maintenance logs were kept in bound notebooks with numbered pages. The entries made in the laboratory book included sample number, sample type, date sample was received, date of analysis, results of analysis, and analyst.

The raw analytical data were stored in electronic files, and hard copies of the run data and chromatograms will be kept indefinitely.

VII. PERFORMANCE AUDITS

Flow Rate Audit

The flow rate of each sampler used for the monitoring was audited on July 8, 1994, following the procedures outlined in Attachment I. The audit was conducted with a 0 to 3 lpm mass flow meter traceable to the National Institute of Standards and Technology (NIST). The difference between the reported and true flow rates averaged 0.46% and ranged from -3.14% to 1.65% (Table 1).

Table 1. Results of the flow rate audit of the samplers used in the monitoring of azinphos methyl.

Sampler Number	Reported Flow (LPM)	True Flow (LPM)	Percent Difference
1A	11.85	1.82	1.65
1B	1.85	1.85	0.00
2A	1.85	1.83	1.09
2B	1.85	1.88	-1.60
3A	1.85	1.87	-1.07
3B	1.85	1.91	-3.14
4A	1.85	1.83	1.09
4B	1.85	1.84	0.54
5A	1.85	1.89	-2.12
5B	1.85	1.87	-1.07

$$\text{Percent Difference} = \frac{\text{Reported Flow} - \text{True Flow}}{\text{True Flow}} \times 100$$

Laboratory Performance Audit

The accuracy of the analytical method was evaluated by submitting for analysis a set of seven audit samples spiked with measured amounts of azinphos methyl. The samples were prepared by QAS staff on August 16, 1994, following the procedures outlined in Attachment II, and they were extracted and analyzed on August 18. The difference between the assigned and the reported total mass of azinphos methyl averaged -32% with a range of -35% to -27% (Table 2).

Table 2. Results of analyses of the azinphos methyl audit samples.

Sample ID	Assigned Mass (ug)	Reported Mass (ug)	Percent Difference
AZM-1	0.832	0.56	-33
AZM-2	0.312	0.22	-30
AZM-3	0.000	N/D	N/A
AZM-4	0.521	0.34	-35
AZM-5	0.312	0.21	-33
AZM-6	0.832	0.55	-34
AZM-7	0.521	0.38	-27

$$\text{Percent Difference} = \frac{\text{Reported Mass} - \text{Assigned Mass}}{\text{Assigned Mass}} \times 100$$

ATTACHMENT I

Flow Rate Audit Procedures for Air Samplers Used in Pesticide Monitoring

Introduction

Air samplers are audited using a calibrated differential pressure gauge or a mass flow meter that is standardized against a NIST traceable flow calibrator. The audit device is connected in series with the sampler's flow meter, and the flow rate is measured while the sampler is operating under normal sampling conditions. The sampler's indicated flow rate is corrected based on its calibration, and the true flow is calculated from the audit device's calibration curve. The sampler's corrected flow is then compared to the true flow, and a percent difference is determined.

Equipment

The basic equipment required for the air sampler flow audit is listed below. Additional equipment may be required depending on the particular configuration and type of sampler.

1. NIST-traceable mass flow meter.
2. Calibrated differential pressure gauge with laminar flow element.
3. 1/4" O.D. Teflon tubing.
4. 1/4", stainless steel, Swagelock fittings.

Audit Procedures

1. If power is available, connect the mass flow meter into a 110 VAC outlet, and allow it to warm up for at least ten minutes. Otherwise, perform the audit with the calibrated differential pressure gauge.
2. Connect the inlet port of the audit device to the outlet port of the sampler's flow control valve with a 5 ft. section of Teflon tubing and Swagelock fittings.
3. Connect the outlet port of the audit device to the pump with another 5 ft. section of Teflon tubing and Swagelock fittings.
4. Allow the flow to stabilize for at least 1-2 minutes and record the flow rate indicated by the sampler and the audit device's response.
5. Calculate the true flow rate from the audit device's response and record the results. Obtain the corrected sampler flow rate from the field operator. Calculate the percent difference between the true flow rate and the corrected measured flow rate.

ATTACHMENT II

Performance Audit Procedures
for the Laboratory Analysis of Azinphos Methyl

Introduction

The purpose of the laboratory performance audit is to assess the accuracy of the analytical methods used by the laboratory measuring the ambient concentrations of azinphos methyl. The audit is conducted by submitting audit samples spiked with known concentrations of azinphos methyl. The analytical laboratory reports the results to the Quality Assurance Section, and the difference between the reported and the assigned concentrations is used as an indicator of the accuracy of the analytical method.

Materials

1. Azinphos methyl, 98% pure, Chem Service, Lot: 127-141A
2. Ethanol
3. XAD-2 adsorbent tubes, 600 mg, SKC, Lot: 816

Safety Precautions

Prior to handling any chemical, read the manufacturer's Material Safety Data Sheets (MSDS). Avoid direct physical contact with chemicals. Avoid breathing vapors. Use only under a fume hood. Wear rubber gloves, safety glasses, and protective clothing.

Preparation of a 4 mg/ml Azinphos Methyl Stock Solution

Weigh 40 mg of azinphos methyl into a clean 10 ml volumetric flask. Dissolve with ethanol and dilute to the mark. Correct for the purity of azinphos methyl and record the concentration.

Preparation of a 0.02 mg/ml Azinphos Methyl Spiking Solution

Transfer 50 ul of the azinphos methyl stock solution into a clean 10 ml volumetric flask. Dilute to the mark with ethanol.

Preparation of Audit Samples

Prepare seven audit samples by spiking XAD-2 adsorbent tubes with the volume of azinphos methyl spiking solution indicated in the table below. Using a microsyringe, insert the needle into the primary section of the XAD-2 tube, and push the plunger slowly while rotating the tube. Avoid contact of the spiking solution with the tube walls.

Sample ID	Azinphos Methyl Spiking Solution Volume (ul)
AZM-1	40.0
AZM-2	15.0
AZM-3	0.0
AZM-4	25.0
AZM-5	15.0
AZM-6	40.0
AZM-7	25.0